In the Specification

Before paragraph [0001], kindly insert the following:

RELATED APPLICATION

This is a §371 of International Application No. PCT/JP2005/001039, with an international filing date of January 20, 2005 (WO 2005/070997 A1, published August 4, 2005), which is based on Japanese Patent Application No. 2004-014128, filed January 22, 2004.

Kindly replace paragraphs [0002] and [0003] with the following:

BACKGROUND ~~ART~~

Polyols usable as component materials for producing polyurethane resins and polyester resins are heretofore usually selected from polyetherdiols and polyesterdiols. Currently, however, it is known that polycarbonatediols are useful as materials for resins having excellent heat resistance, hydrolysis resistance and weathering resistance and, thus, have drawn industrial attention. Also, it is known that the polycarbonate resins have high stiffness and low elongation and thus the polycarbonate resins exhibit an insufficient flexibility in comparison to that of the conventional resins, particularly polyether resins. Also, the conventional polycarbonate resins have a problem that the glass transition temperature thereof is too high and the low temperature characteristics thereof are insufficient. To solve the above-mentioned problems, it is proposed to utilize, as a polyol, a polycarbonate diol having an ether group introduced into the molecule of the polyol, namely, a polyethercarbonatediol.

The diol component of the polyethercarbonatediol includes, for example, mixed diols comprising a diol compound comprising, as a component, a polycarbonate chain (particularly 1,6-hexanediol-polycarbonateglycol) with a compound having a ethyleneoxide structures; or a polymeric diol compound ~~(Patent Reference 1)~~as disclosed in JP-59-66577-A, for example, a block copolymer

comprising, in a molecule thereof, as principal components, polycarbonate chains and ethylene oxide structural units; and polyetherdiol compounds produced by etherifying 1,6-heanediol ~~(Patent Reference 2)~~as disclosed in JP -63-305127-A or a mixture of a polyethylpolyol (for example, diethylene glycol, triethylene glycol, tetraethylene glycol, tripropylene glycol, polypropylene glycol or polytetramethylene glycol) with a polyhydric alcohol (for example, ethylene glycol, 1,2-propanediol, 1,3-butanediol, or 1,6-hexanediol ~~(Patent Reference 3)~~as disclosed in JP -2-255822-A.

Kindly replace paragraphs [0005] through [0021] with the following:

Also, ~~Patent Reference 4~~JP-2002-256069-A discloses that, as a diol component for the polyethercarbonatediol, diol compounds produced by a reaction of 1,6-hexanediol with ethyleneoxide and/or 1,2-polypyleneoxide can be used. The polyethercarbonatediol produced from the above-mentioned diol compounds is a low viscosity liquid which can be easily handled, and the resultant polyurethane resin comprising, as a diol component, the above-mentioned polyethercarbonate diol exhibits good low temperature characteristics. However, the thermoplastic polyetherpolymethanes produced from the polyetherdiols exhibit an ultimate elongation which is not always high enough to the requirements of practical use.

~~[Patent Reference 1] JP-59-66577-A~~

~~[Patent Reference 2] JP-63-305127-A~~

~~[Patent Reference 3] JP-2-255822-A~~

~~[Patent Reference 4] JP-2002-256069-A~~

~~DISCLOSURE OF INVENTION~~SUMMARY

~~An object of the present invention is to solve the above-mentioned problems of the prior art and to~~We provide a liquid polyethercarbonatediol compound having a low viscosity, easy handling, a low glass transition temperature, a high elongation, an excellent low temperature characteristics and

a high flexibility and being useful as a material for thermoplastic polyurethane resin, and a thermoplastic polyurethane produced from the above-mentioned diol compound.

~~The object of the present invention is attained by the liquid polyethercarbonatediol compound and the thermoplastic polyurethane produced from the diol compound of the present invention.~~

The liquid polyethercarbonatediol compound ~~of the present invention~~ comprises a reaction product of

(1) a carbonate ester compound,

with

(2) a polyetherdiol compound comprising (A) at least one type of structural units represented by the formula (a):

-RO- (a)

in which formula (a), R represents a member selected from unsubstituted linear alkylene groups having 3 to 5 carbon atoms and substituted alkylene groups each constituted from a linear alkylene backbone chain having 3 to 5 carbon atoms and at least one alkyl side chain attached to the backbone chain and having 1 to 4 carbon atoms, and (B) at least one type of structural units selected from those represented by the formulae (b) and (c):

$-(CH_2)_2-O-$ (b)

and

$-CH_2CH(CH_3)-O-$ (c),

wherein an average molar number n of the structural units of the formula (b) and an average molar number of m of the structural units of the formula (c) each per mole of the structural units of the formula (a) contained in the polyetherdiol compound (2) are, respectively and independently from each other, a positive number satisfying the requirements:

$$0 \leq n \leq 5$$

and

$$0 \leq m \leq 5,$$

and the sum (n + m) of the average molar numbers n and m of the structural units of the formulae (b) and (c) is a positive number satisfying the requirement:

$$1 < (n + m) \leq 5.$$

In the liquid polyethercarbonatediol compound ~~of the present invention~~, in the polyetherdiol compound (2), the average molar number m of the structural units of the formula (c) per mole of the structural units of the formula (a) is preferably zero.

In the liquid polyethercarbonatediol compound ~~of the present invention~~, the polyetherdiol compound (2) is preferably selected from addition reaction products of (i) at least one member selected from unsubstituted and substituted 1,3-propanediol, unsubstituted and substituted 1,4-butanediols, and unsubstituted and substituted 1,5-pentanediols, each of which substituted compounds has at least one alkyl group having 1 to 4 carbon atoms and attached to the alkylene group of the substituted compound, with (ii) at least one member selected from ethyleneoxide and propyleneoxide.

In the liquid polyethercarbonatediol compound ~~of the present invention~~, the polyetherdiol compound (2) preferably has a number average molecular weight of 100 to 500.

The liquid polyestercarbonatediol compound ~~of the present invention~~ preferably has a number average molecular weight in the range of from 400 to 5000.

In the liquid polyethercarbonatediol compound ~~of the present invention~~, the carbonate ester compound (1) is preferably selected from dialkyl carbonates, diary carbonates, alkylene carbonates and alkylaryl carbonates.

The thermoplastic polyurethane ~~of the present invention~~ comprises an addition reaction product of a diol component comprising at least one liquid polyethercarbonatediol compound of the present invention, with a polyisocyanate compound component comprising at least one polyisocyanate compound and with a chain extender.

In the thermoplastic polyurethane ~~of the present invention~~, the polyisocyanate compound is preferably selected from 1,3-trimethylenediisocyanate, 1,4-tetramethylenediisocyanate, 1,6-hexamethylenediisocyanate, 2,2,4-trimethylhexamethylenediisocyanate, 2,4,4-trimethylhexamethylenediisocyanate, 1,9-nonamethylenediisocyanate, 1,10-decamethylenediisocyanate, 1,4-cyclohexanediisocyanate, isophoronediisocyanate, 4,4'-dicyclohexylmethanediisocyanate, 2,2'-diethyletherdiisocyanate, hydrogenated xylenediisocyanate, hexamethylenediisocyanate-biuret compound, p-phenylenediisocyanate, tolylenediisocyanate, xylylenediisocyanate, 4,4'-diphenyldiisocyanate, 1,5-naphthalenediisocyanate, 4,4'-diphenylmethanediisocyanate, 3,3'-methyleneditolylene-4,4'-diisocyanate, tolylenediisocyanate-trimethyllol propane aduct, triphenylmethanetriisocyanate, 4,4'-diphenyletherdiisocyanate, tetrachlorophenylenediisocyanate, 3,3'-dichloro-4,4'-diphenylmethanediisocyanate, and triisocyanatephenylthiophosphate.

In the thermoplastic polyurethane ~~of the present invention~~, the chain extender preferably comprises at least one member selected from ethyleneglycol, 1,2-propyleneglycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, neopentyl glycol, 3-methyl-1,5-pentanediol, 3,3-dimethylolheptane, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, 1,4-dihydroxyethylcyclohexane, ethylenediamine, 1,2-propylene-diamine, 1,6-hexamethylenediamine, isophoronediamine, bis(4-aminocyclohexyl)methane, piperazine, meta- or para-xylylenediamine, 2-ethanolamine, N-methyldiethanolamine, N-phenyldipropanolamine, hydroxyethylsulfamide, hydroxyethylaminoethylsulfamide, urea and water.

~~In the present invention, the~~The term "liquid polyethercarbonatediol compound" includes a group of polyethercarbonatediol compounds which are in the state of a liquid and exhibit a fluidity at room temperature, namely from about 5°C to about 30°C.

~~The present invention enables~~Our efforts enable the liquid polyethercarbonatediol compound and thermoplastic polyurethane in which the polyethercarbonatediol compound is contained as a diol component~~, which can solve the problems of the prior art,~~ to be provided. Namely, the liquid polyethercarbonatediol compound ~~of the present invention~~ has a low viscosity and can be easily handled, and by utilizing the diol compound as a diol component, thermoplastic polyurethanes having excellent low temperature characteristics, flexibility and stretchability (elongation and deformation recovery can be provided. The thermoplastic polyurethane ~~of the present invention~~ has the above-mentioned excellent properties and further excellent heat resistance, hydrolysis resistance and weather resistance, and thus is well balanced in the above-mentioned properties, and thus is useful as materials for thermoplastic elastomers, elastic fibers, and artificial leathers.

~~BEST MODE OF CARRYING OUT THE INVENTION~~DETAILED DESCRIPTION

The liquid polyethercarbonatediol compound ~~of the present invention~~ comprises a reaction product of a carbonate ester compound (1) with a polyetherdiol compound (2).

The polyetherdiol compound (2) comprises:

(A) at least one type of structural units represented by the formula (a):

-RO- (a)

in which formula (a), R represents a member selected from unsubstituted linear alkylene groups having 3 to 5 carbon atoms and substituted alkylene groups each constituted from a linear alkylene backbone chain having 3 to 5 carbon atoms and at least one, preferably one or two alkyl side chains attached to the backbone chain and each having 1 to 4 carbon atoms, and

(B) at least one type of structural units selected from those represented by the formulae (b) and (c):

$$-(CH_2)_2-O- \qquad (b)$$

and

$$-CH_2CH(CH_3)-O- \qquad (c),$$

wherein an average molar number n of the structural units of the formula (b) and an average molar number of m of the structural units of the formula (c) each per mole of the structural units of the formula (a) contained in the polyetherdiol compound (2) are, respectively and independently from each other, a positive number satisfying the requirements:

$$0 \leq n \leq 5, \text{ preferably } 1 \leq n \leq 3$$

and

$$0 \leq m \leq 5, \text{ preferably } 1 \leq m \leq 3$$

and the sum (n + m) of the average molar numbers n and m of the structural units of the formulae (b) and (c) is a positive number satisfying the requirement:

$$1 < (n + m) \leq 5, \text{ preferably } 1 \leq (n + m) \leq 3.$$

The polyetherdiol compound usable for the production of the liquid polyethercarbonatediol compound ~~of the present invention~~ may comprise the structural units (A) represented by the formula (a) and the structural units (B) consisting of only the structural units represented by the formula (b), and the content (average molar number m) of the structural units (C) represented by the formula (c) per mole of the structural units (A) represented by the formula (a) may be zero. In this case, in the formula (a) representing the structural units (A), R represents an unsubstituted linear alkylene backbone group having 3 to 5 carbon atoms or a substituted alkylene group constituted from a linear alkylene backbone group having 3 to 5 carbon atoms and at least one, preferably 1 or 2 alkyl side

chains attached to the backbone chain and having 1 to 4 carbon atoms; and the average molar number n of the structural units represented by the formula (b) per mole of the structural units represented by the formula (a) contained in the polyetherdiol compound (2) satisfies the requirement:

$1 < n \leq 5$, preferably $1 < n \leq 3$.

Kindly replace paragraphs [0023] and [0024] with the following:

In the polyethercarbonatediol compound ~~of the present invention~~, the unsubstituted alkylene group represented by R in the formula (a) and having 3 to 5 carbon atoms includes propylene group (trimethylene group), butylene group (tetramethylene group), and pentylene group (pentamethylene group), and the alkyl group contained, as a substituent group, in the substituted alkylene group and having 1 to 4 carbon atoms is selected from methyl, ethyl, propyl, isopropyl, butyl and isobutyl groups.

The polyetherdiol compounds usable for the production of the liquid polyethercarbonatediol compound ~~of the present invention~~, for example, those comprising the structural units (a) and the structural units (b) and/or (c), includes the compounds represented by the general formulae (i) to (vii). Also, the compounds comprising the structural units (a) and the structural units (b) and/or (c) include those comprising the structural units (b) and (c) located in the structural units (b) or (c) in the above-mentioned general formulae (i) to (vii)~~.~~:

$HO\text{-}(b)_n\text{-}(a)\text{-}(c)_m\text{-}OH$ (i)

$HO\text{-}(b)_{n1}\text{-}(a)\text{-}(b)_{n2}\text{-}OH$ (ii)

$HO\text{-}(c)_{m1}\text{-}(a)\text{-}(c)_{m2}\text{-}OH$ (iii)

$HO\text{-}(a)\text{-}(b)_n\text{-}(c)_m\text{-}OH$ (iv)

$HO\text{-}(a)\text{-}(c)_m\text{-}(b)_n\text{-}OH$ (v)

$HO\text{-}(a)\text{-}(b)_n\text{-}OH$ (vi)

$HO\text{-}(a)\text{-}(c)_m\text{-}OH$ (vii).

Kindly replace paragraphs [0027] through [0029] with the following:

The polyetherdiol compound ~~usable for the present invention~~ may be produced by a method in which a reactor is charged with at least one type of the above-mentioned diol compound and a catalyst comprising a basis alkali metal compound (preferably an alkali metal hydroxide, etc.); while ethylene oxide and/or propylene oxide is continuously fed into the reactor, the diol compounds and the alkylene compounds are reacted at a temperature of 80 to 150°C under a pressure of 49 to 490 kPa (0.5 to 5 kg/cm^2), until the molecular weight of the reaction product reaches a desired level corresponding to the desired n and m values; and the reaction product is subjected to after treatments, for example, neutralization, dehydration, drying and filtration. The after treatments may consist of water-rinsing and drying only, and the after treatments may be carried out in combination with absorption and/or distillation treatment for removal of the catalyst.

The alkylene diol for the production of the polyethercarbonatediol compound ~~of the present invention~~ may be employed in combination with at least one member selected from unsubstituted alkylene diol comprising 6 or more, preferably 6 to 12 carbon atoms and substituted alkylene diols containing an alkyl substituent group having carbon atoms in the same number as that mentioned above and attached to the alkylene backbone chain of the alkylene diol.

The amount of the alkylene diol for the combination use together with the alkylene diol compound for the production of the polyetherdiol compound ~~for the present invention~~, is preferably 50 molar% or less of the alkylene diol compound.

Kindly replace paragraphs [0031] through [0035] with the following:

The polyetherdiol compound ~~usable for the present invention~~ preferably has a number average molecular weight of 100 to 500, more preferably 120 to 400.

In the above-mentioned polyetherdiol compounds ~~usable for the present invention~~, those (for example, represented by the general formulae (ii) or (vi)) comprising the structural units (a) and the structural units (b) but not the structural units (c), namely, satisfying $m = 0$, and $1 < n \leq 5$, are preferably employed. Namely, the preferably polyetherdiol compounds ~~for the present invention~~ are those having the structural units (a) and the structural (b) but not the structural units (c), namely, $m = 0$ and $1 < n \leq 5$; represented by the general formulae (ii) or (vi); and having a number molecular weight of 100 to 500, more preferably 120 to 400.

In the polyetherdiol compounds ~~usable for the present invention~~, those having the structural units in which R preferably represents a straight alkylene chain having carbon atoms of 3 to 5 and free from subsistents, more preferably a trimethylene group, are particularly preferred.

The carbonate esters compound (1) ~~usable for the present invention~~ include aliphatic, aromatic and aromatic group-containing aliphatic carbonate esters, for example, dialkyl carbonates, diaryl carbonates, alkylene carbonates. The aliphatic carbonates may be cycloaliphatic carbonates. Practically preferable carbonate esters are, for example, dimethyl carbonate, diethyl carbonte, di-n-butyls carbonate, diisobutyl carbonate, diphenyl carbonate, methylphenyl carbonate, ethylene carbonate, propylenecarbonate.

The reaction of the polyetherdiol compound (2) with the carbonate ester compound (1) may be carried out in accordance with the conventional method for producing a polycarbonatediol. Namely, the liquid polyethercarbonatediol compound ~~of the present invention~~ can be produced by subjecting the polyetherdiol compound (1) and the carbonate ester compound (2) to a transesterification reaction in the presence of a transesterification catalyst while a by-product, namely an aliphatic or aromatic alcohol, is continuously withdrawn to the outside of the reaction system.

Kindly replace paragraphs [0040] through [0044] with the following:

The liquid polyethercarbonatediol compound ~~of the present invention~~ preferably has a number average molecular weight in the range of from 400 to 5000, more preferably from 500 to 3000. Accordingly, the molecular weight of the liquid polyethercarbonatediol compound is preferably controlled by a conventional method, for example, in the case where the hydroxyl value (namely the molecular weight) of the reaction product falls outside of the target range, namely, the number average molecular weight of the reaction product is less than 400, the polyetherdiol compound is further reacted while distilling the polyetherdiol compound under reduced pressure; and in the case where the number average molecular weight of the resultant product is more than 5,000, an additional amount of the polyetherdiol compound is added to the reaction system and further transesterification-reacted. Also, if necessary, after the molecular weight is adjusted, the residual transesterification catalyst in the resultant liquid polyethercarbonatediol compound is preferably deactivated with a phosphorus compound (for example, phosphoric acid, butyl phosphorate or dibutyl phosphorate). The liquid polyethercarbonatediol compound of the present invention can be obtained by the above-mentioned procedures.

In the production of the liquid polyethercarbonatediol compound ~~of the present invention~~, particularly preferably, a polyetherdiol compound comprising by the structural units (a) and the structural units (b) but not the structural units (c), namely, $m = 0$ and $1 < n \leq 5$, is reacted with a carbonate ester compound.

Further preferably, the structural units (a) in which R represents a straight alkylene chain group are preferred, more preferably, R represents a trimethylene group. Namely, in the reaction ~~for the present invention~~, preferably the diol component comprising a polyetherdiol compound having the structural units (a) in which R represents a trimethylene group) and the structural units (b) but not

the structural units (c) and having m = 0, $1 < n \leq 5$, is reacted with a carbonate ester component to produce a liquid polyethercarbonatediol compound having, preferably, a number average molecular weight of 400 to 5,000, more preferably 500 to 3,000. In this case, the polyether diol compound having the above-mentioned appropriate number average molecular weight of 100 to 500 is preferably employed.

The thermoplastic polyurethane ~~of the present invention~~ is produced by subjecting a diol component which comprises at least one type of liquid polyethercarbonatediol compound ~~of the present invention~~, at least one type of polyisocyanate compound and a chain-extender to a reaction and, namely, to a polyurethane-producing reaction.

The polyisocyanate compound ~~usable for the present invention~~ can be selected from various polyisocyanates, for example, aliphatic (including cycloaliphatic) and aromatic diisocyanates. The aliphatic diisocyanates are preferably selected from, for example, 1,3-trimethylenediisocyanate, 1,4-tetramethylenediisocyanate, 1,6-hexamethylenediisocyanate, 2,2,4-~~trimethylhexamthylenediiso-cyanate~~trimethylhexamethylenediisocyanate, 2,4,4-~~trimethylhexamthylenediisocyanate~~trimethyl-hexamethylenediisocyanate, 1-9-novamethylenediisocyanate, 1,10-decamethylenediisocyanate, 1,4-cyclohexanediisocyanate, isophoronediisocyanate, 4,4-dicyclohexylmethanediisocyanate, 2,2'-diethyletherdiisocyanate, hydrogenated xylylenediisocyanae and hexamethylenediisocyanate-biuret compound.

Kindly replace paragraph [0047] with the following:

The chain extender usable for the polyurethane ~~of the present invention~~ preferably comprises a low molecular weight compound having at least two hydrogen atoms capable of reacting with the isocyanate group. As a compound usable for the chain extender, a polyol and a polyamine are preferably employed. The chain extender includes aliphatic diols (including cycloaliphatic diols), for

example, ethyleneglycol, 1,2-propyleneglycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, neopentylglycol, 3-methyl-1,5-pentanediol, 3,3-dimethylolheptane, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, and 1,4-dihydroxyethylcyclohexane; aliphatic and aromatic diamines, for example, ethylenediamine, 1,2-propylenediamine, 1,6-hexamethylenediamine, isophoronediamine, bis(4-aminocyclohexyl)methane, piperazine and meta(or para)-xylylenediamine; aliphatic or aromatic aminoalcohols, for example, 2-ethanolamine, N-methyldiethanolamine, and N-phenyldipropanolamine; hydroxyalkylsulfamides, for example, hydroxyethylsulfamide and hydroxyethylaminoethylsulfamide; and urea and water. Among the above-mentioned compounds for the chain extender, 1,4-butanediol, 2-ethanolamine and 1,2-propylene diamine are more preferably employed. The compounds for the chain extender may be employed alone or in a mixture of two or more thereof.

Kindly replace paragraphs [0053] through [0054] with the following:

The thermoplastic polyurethane ~~of the present invention~~ produced by the above-mentioned methods has molecular terminals which may be any of a hydroxyl group and an isocyanate group. The thermoplastic polymethane ~~of the present invention~~ can have a further increased molecular weight or a network structure by further reacting with a compound having at least two hydrogen atoms reactive to the isocyanate group or a compound having at least two isocyanate group. A closs-linkage structure can be introduced into the thermoplastic polyurethane ~~of the present invention~~ by further reacting the thermoplastic polyurethane with a compound having urethane bond and/or urea bond or a compound having at least three hydrogen atoms reactive to the isocyanate group. Further, the thermoplastic polyurethane may employed in combination with a conventional additive unless the combination hinders the effect ~~of the present invention~~.

Examples

~~The present invention~~Selected aspects of this disclosure will be further explained by the following examples and comparative examples.

Kindly replace paragraphs [0099] and [0100] with the following:

In view of the examples and comparative examples shown above, when the liquid polyethercarbonatediols of ~~the present invention~~this disclosure and the conventional polyetherdiol compounds having the same molecular weight as each other are compared with each other, the liquid polyethercarbonatediols of ~~the present invention~~this disclosure have a low viscosity and a low glass transition temperature compared to the conventional polyetherdiol compounds, the thermoplastic polyurethanes prepared from the polyethercarbonatediol of ~~the present inventions~~this disclosure have a low glass transition temperature similar to that of the conventional thermoplastic polyurethanes and a clearly higher ultimate elongation than that of the conventional polymethane. Also, the thermoplastic polyurethanes produced from the polyethercarbonatediols of ~~the present invention~~this disclosure exhibit satisfactory flexibility and stretchability. Further the thermoplastic polyurethanes produced from the liquid polyethercarbonatediols of ~~the present invention~~this disclosure exhibit a very high weather resistance in comparison with that of the thermoplastic polyurethane produced from the conventional polyetherdiol compounds.

INDUSTRIAL UTILIZABILITY

The liquid polyethercarbonatediol ~~of the present invention~~ is useful as a material for production of polymethanes, polyesters, etc., and usable as a polymeric modifier and a polymeric plasticizer. Also, the thermoplastic polyurethane ~~of the present invention~~ is useful as a material for the production of thermoplastic elastomers, elastic fibers and artificial leathers.